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Orientation of Aromatic Ion Exchange Diamines and the Effect on Melt Viscosity and Thermal Stability of PMR-15/ Silicate Nanocomposites

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Abstract

Nanocomposites of PMR-15 polyimide and a diamine modified silicate were prepared by addition of the silicate to the PMR-15 resin. The orientation of the ion exchange diamine within the silicate gallery was determined by x-ray diffraction and found to depend on the clay cation exchange capacity. The oligomer melt viscosity exhibited a dependence on the orientation of the diamine in the silicate interlayer, and in some cases, on the length of the diamine. A correlation was observed between the oligomer melt viscosity and the crosslinking enthalpy, where nanocomposites with an increased melt viscosity exhibited a decrease in enthalpy on crosslinking. After crosslinking, those nanocomposites with a high melt viscosity had poorer thermal oxidative stability compared to the less viscous systems. The melt viscosity was tailored by co-exchange of an aromatic diamine and an aliphatic amine into the silicate. Nanocomposites prepared with this silicate exhibited an increase in thermal oxidative stability compared to the neat resin.

Introduction

The durability and reliability of materials used in aerospace components is a critical concern. Many of these applications, in particular those in propulsion components, require a high glass transition temperature (T_g), high temperature stability in a variety of environments, and good mechanical properties over a wide range of temperatures.¹ PMR (Polymerization of Monomer Reactants)-type polyimides are thermosetting polymers which combine excellent processability, mechanical properties, and thermal oxidative stability (TOS). PMR-15 is commercially available and prepared in two stages from three monomer reactants: 2-carbomethoxy-3-carboxy-5-norbornene (nadice ester, NE), 4,4'-methylenedianiline (MDA), and the dimethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid (BTDE). Curing under heat and pressure results in a highly crosslinked network structure.² There has been a significant amount of research aimed at increasing the TOS of PMR-15 by altering the structure of the diamine,² the dianhydride,³ or the end-cap⁴. An alternative to modification of the polymer, as a means of increasing TOS, is the dispersion of a layered silicate in the polymer matrix.

Layered silicates have quickly become recognized as useful fillers in polymer matrix composites. Their platelet morphology and high aspect ratio results in greatly improved thermal,⁵ mechanical,⁶ and barrier properties.⁷ A number of papers have reported improvements in the physical properties of thermoplastic polyimide nanocomposites.⁸ However, the majority of work in thermosetting polymers has focused on epoxy systems.⁹ The purpose of the work described in this paper was to investigate the TOS of PMR-15 nanocomposites. Specifically this research was focused on the relationship between the ion exchange diamine chain length and orientation, including its effect on the oligomer melt viscosity and the polymer crosslink density.

Experimental

Bentonite (Bentolite-H, cation exchange capacity (CEC) = 90 meq/100g) was received from Southern Clay Products and will be referred to as SCP throughout this paper. Montmorillonite (PGV-grade, CEC = 145 meq/100g) was received from Nanocor and will be referred to as PGV.

PMR-15 resins were fabricated in several steps, as illustrated in Figure 1. The monomers were dissolved in methanol (50 wt%) followed by solvent evaporation, on a hot plate, at 60° to 70°C. B-staging the mixture at 204° to 232°C in an air circulating oven produced a mixture of low molecular weight imide oligomers. The oligomer mixture was then cured in a mold at 315°C under 2355 psi to produce the crosslinked polymer. The polymer was post cured in an air circulating oven for 16 hours at 315°C to further crosslinking. The average number of imide rings was kept constant by using a stoichiometry of 2NE/ (n+1)MDA/ nBTDE (n=2.087) corresponding to an average molecular weight of 1500.¹⁰ The method used in the preparation of PMR-15 nanocomposites was identical to that used for the neat resin, except that the organically modified silicate (1 wt% to 7 wt%) was added to the methanol solution of the monomers.

Aromatic diamines were used for ion exchange. They included: *p*-phenylene diamine (pPDA), methylene dianiline (MDA), 4,4'-(1,4-phenylene-bismethylene) bisaniline (BAX), and 4,4'-bis(4-aminobenzyl)diphenylmethane (MMM). Ion exchange of the interlayer cations of SCP and PGV clays with the protonated forms of the listed amines was performed by dissolving the amine (5mmol) in 450 mL of a 0.005M aqueous HCl solution at 60°C. In the case where the diamine did not dissolve in the aqueous solution, ethanol (25 – 50 mL) was added. The silicate (5g) was dispersed in the solution and the resultant mixture was stirred at 60°C for three hours. The solution was filtered and the clay was washed thoroughly with warm water. To maximize the amount of diamine exchanged, the procedure was repeated by addition of the organically modified silicate to a new solution of protonated amine. A total of three exchange reactions were completed for each silicate/ amine system.¹¹ The silicate was then dried overnight in a vacuum oven at 100°C. Throughout this paper, the clays modified with various amines will be identified by the silicate and the ion exchange amine, for example, SCP-amine or PGV-amine for the organically modified forms of SCP and PGV respectively.

The melt viscosities of B-staged nanocomposites were compared by measurement of the materials' squeeze flow index (SFI).¹² Comparison of the SFI gives a relative indication of the melt flow. The powders (0.5g) were cold pressed into a pellet. The pellet was placed between Kapton sheets in a 25 ton press and held at 315°C and 200 psi for two minutes. This process resulted in a circular "splat" of resin, due to the resin flow. The diameter of the "splat" was measured in several places and the average was used to calculate the area of resin flow. Each sample was run in triplicate.

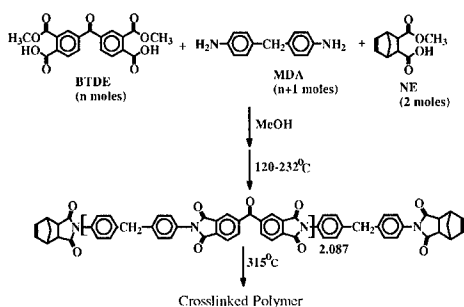


Figure 1. PMR-15 synthesis

Results and Discussion

The aromatic diamines chosen as the ion exchange material were similar in chemical structure to, or the same as, the diamine found in PMR-15. Tethering one end of the diamine to the silicate leaves the second free for reaction with BTDE during PMR-15 synthesis. Wei *et al.*⁸ demonstrated this as a viable method of achieving irreversible swelling of the silicate in a thermoplastic polyimide matrix.

The d-spacing of the organically modified silicates was calculated from x-ray diffraction (XRD) data. The investigated diamines and the XRD patterns of SCP exchanged with each diamine are shown in Figure 2. The d_{001} peak of untreated SCP appears at $2\theta = 7.07^\circ$ ($d_{001} = 1.25$ nm). Ion exchange with pPDA shifts the peak to $2\theta = 5.97^\circ$ ($d_{001} = 1.48$ nm). After this initial increase in gallery height, there is little change in d-spacing as the number of phenylene linkages in the diamine increases. Unlike SCP, ion exchange in PGV produces a monotonic increase of the d-spacing with increasing diamine length.

The observed variation in d-spacing between organically modified SCP and PGV suggests that the exchange diamines may adopt a separate configuration in each silicate. Organically modified SCP shows little change in gallery height on increasing the length of the diamine, suggesting that the longer diamines adopt a folded conformation within the silicate gallery. The increase in d-spacing that is observed on ion exchange with PGV suggests the aromatic diamines are not folding, but may extend away from the silicate surface. However, the increase in gallery spacing is small and therefore the chains are likely not perpendicular to the silicate, but may lie at an inclined angle with respect to the silicate surface.

The clays differ in CEC (PGV = 145 meq/100g, SCP = 90 meq/100g) therefore fewer diamines can be exchanged with SCP. It has been shown that the orientation of alkyl ammonium cations within a silicate gallery is dependent on the chain length and layer charge density of the clay.^{13, 14} Due to the low CEC of SCP, there is a large surface area available to the chains so that they may fold back toward the silicate sheet. As the CEC increases, the chain packing density of the exchange diamines increases and the available surface area decreases. This may prevent folding and force the diamines away from the silicate surface, resulting in the observed dependence of PGV d-spacing on the aromatic chain length.

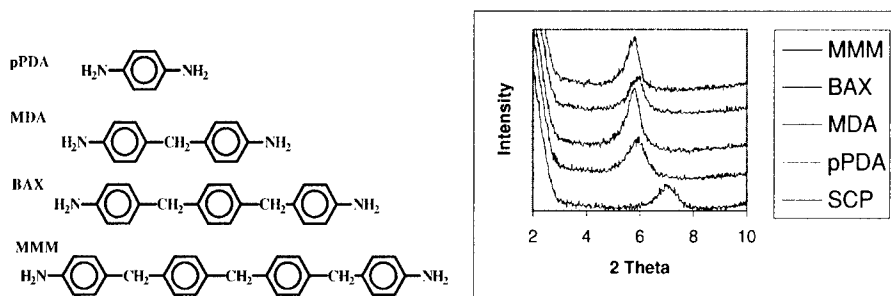


Figure 2. Structures of the diamines used in ion exchange and the XRD patterns of unmodified SCP (bottom pattern) and SCP organically modified with pPDA, MDA, BAX and MMM.

A comparison of the amount of exchanged diamine was made by thermogravimetric analysis (TGA).¹⁵ Measurement of the weight loss on heating the untreated clays to 800°C gives the content of adsorbed and structural water within each clay. Heating the organically modified clays to 800°C, and subtracting out the weight loss corresponding to water content, gives an indication of the amount of diamine present. TGA measurements suggest that an average of 33% more diamine by weight was exchanged into PGV, which is consistent with the difference in the CEC of each clay. An exception is the ion exchange of pPDA, where approximately 18% by weight more diamine is exchanged into SCP.

PMR-15/ silicate nanocomposites were prepared using either modified SCP or PGV. The silicate dispersion was evaluated by XRD and transmission electron microscopy (TEM). All systems showed primarily exfoliated silicate layers with regions of intercalation evident in TEM. The SFI data shown in Table I reveals an increase in the oligomer melt viscosity of SCP nanocomposites compared to the neat resin. Nanocomposites prepared using PGV show a similar oligomer melt viscosity increase when the clay has been ion exchanged with pPDA and MDA. However, nanocomposites prepared with the longer chain diamines, PGV-BAX or PGV-MMM, show an identical or an increased SFI. This suggests a similar or even lower oligomer melt viscosity.

The energy released during endcap crosslinking was measured by high pressure differential scanning calorimetry (HP-DSC) for B-staged nanocomposites and is listed in Table 1. HP-DSC thermograms of B-staged SCP nanocomposites show a decrease in the amount of energy released during the crosslinking reaction, compared to the neat resin, with little dependence on the ion exchange diamine. In B-staged PGV nanocomposites there is an increase in the exotherm, compared to neat PMR-15, with the exception of PGV-pPDA.

The data in Table I suggests a correlation between the oligomer melt viscosity and the crosslinking enthalpy. The apparent decrease in crosslinking with increased oligomer melt viscosity suggests that polar interactions between the oligomer and the silicate surface may limit chain mobility and increase the oligomer melt viscosity, thus decreasing the number of crosslinks formed upon curing.

Typically, an advantage of polymer-clay nanocomposites is an improvement in the polymer thermal stability over that of the neat resin. However, PMR-15 is a fairly stable thermosetting polymer. Disruption of its highly crosslinked structure could lead to a reduction in the TOS. Weight loss measurements of the neat resin and the nanocomposites over 1000 hours at 288°C

show a decrease in TOS in all SCP and PGV nanocomposites, with the exception of PGV-MMM nanocomposites. This material has a weight loss approximately equal to PMR-15 and is the only nanocomposite with an oligomer melt viscosity lower than the neat resin.

Since the higher oligomer melt viscosity tends to decrease the nanocomposite TOS, decreasing the melt viscosity of the B-staged PGV-MDA nanocomposite should yield improvements in TOS. To decrease the melt viscosity of B-staged PMR-15/ PGV-MDA, PGV was ion exchanged with 50 mol% MDA and 50 mol% dodecylamine, (C12). The longer chain length of C12 compared to MDA should keep the oligomer from close contact with the silicate, but still allow reaction between the tethered diamine and BTDE.

Table I. SFI and DSC measurements for PMR-15 nanocomposites prepared with modified SCP and PGV clays. The clay concentration was 2 wt%.

Sample (clay modification)	SFI (cm ²) (SCP)	DSC (mcal/mg) (SCP)	SFI (cm ²) (PGV)	DSC (mcal/mg) (PGV)
PMR-15	93.3	13.7	93.3	13.7
PPDA	77.0	12.0	67.83	11.92
MDA	78.5	10.3	82.39	14.5
BAX	81.7	10.4	93.3	14.6
4-ring	73.9	10.7	108.7	15.0

Measurements of the melt viscosity and crosslinking enthalpy for B-staged nanocomposites prepared with the mixed amine demonstrate that the oligomer melt viscosity and crosslink density can be manipulated by introduction of a long chain alkylamine onto the silicate. Figure 3 shows the TOS of the PGV-(MDA-C12) nanocomposites, where the silicate concentration is increased from 1 wt% to 7 wt%. It should be noted that the degradation temperature of the alkylamines is near the processing temperature of PMR-15 so there is a question as to whether these materials degrade during processing. There is ongoing work to address this question. Here it is assumed that the aliphatic amine is present within the silicate during processing and is responsible for the observed decrease in oligomer melt viscosity. Unfortunately, the low molecular weight alkyl amine can act as a plasticizer in the polyimide matrix, reducing the T_g . The T_g of neat PMR-15 as measured by DMA is 345°C. Addition of 2 wt % PGV-MDA results in a small increase to 348°C, where addition of 2 wt% PGV-C12 lowers the T_g to 330°C. Co-exchange of MDA and C12 results in a T_g of 340°C, which is not a significant change in the T_g .

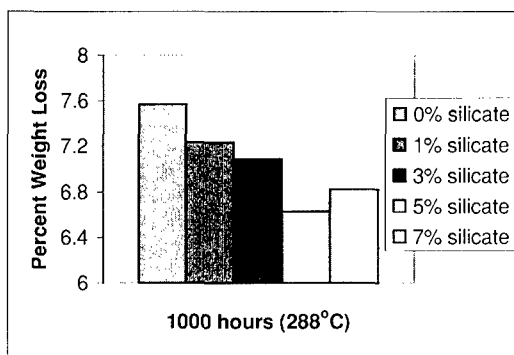


Figure 3. Weight loss of neat PMR-15 and nanocomposites on increasing clay concentration. The silicate is PGV modified with MDA and C12.

Conclusions

The orientation and packing density of the aromatic diamine used to modify bentonite and montmorillonite clays affects the oligomer melt viscosity of a PMR-15/ silicate nanocomposite. An increase in oligomer melt viscosity is accompanied by a decrease in the oligomer crosslinking enthalpy, as well as a decrease in the TOS of the cured nanocomposite. The oligomer melt viscosity can be modified by co-exchange of an aromatic diamine and a long chain alkyl amine on the clay. Incorporation of PGV/(MDA-C12) into the PMR-15 matrix has little effect on T_g . In addition, the TOS of the nanocomposite is improved compared to the neat resin or nanocomposites prepared with clay exchanged only with the aromatic diamine. Thus, use of PMR-15/ silicate nanocomposites is a viable approach to improve high temperature stability.

Acknowledgments

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